JNPS

ISSN 2392-473X
Journal of Nepal Physical Society, August-2015, Vol. 3, No. 1

# Effects of Concentration of Triethanolamine and Annealing Temperature on Band Gap of Thin Film of Tin Sulphide Prepared by Chemical Bath Deposition Method

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**Abstract**

*Thin films of Tin Sulphide (SnS) were deposited by chemical bath deposition technique using a precursor solution of stannous chloride ($SnCl_2.2H_2O$), thioacetamide (TA), triethanolamine (TEA), ammonia ($NH_3$), and distilled water. The effects of concentration of triethanolamine and annealing temperature on the growth of SnS films were studied to optimize the growth conditions. X-ray diffraction study shows the deposited films were polycrystalline in nature and orthorhombic in structure. The optical direct and indirect band gap values of SnS films prepared with 15ml of TEA were found to be 1.76 eV and 0.89 eV respectively. Annealing the sample prepared with 12ml of TEA results increase in band gap from 1.79eV to 3.32eV.*

***Keywords:*** *Thin films, optical band gap, photovoltaic materials, X-ray diffraction*

## 1. Introduction

In recent years, semiconducting thin films of nano-materials have been attracting a lot of attention due to their unique physical and chemical properties which help to enhance device performance [*Anuar et al.,* 2008] Polycrystalline thin films of tin sulphide (SnS) are considered as a potential material for solar cells because of their photovoltaic properties. Tin sulphide is a cost-effective and environmentally friendly material among the group of compound semiconductors that are currently being explored for low-cost photovoltaic materials. It possesses a high optical absorption coefficient which is greater than $10^4$ $cm^{-1}$ [*Ristov et al.,* 1989**].** The physical and optical properties of SnS such as its color and optical band gap depend on the method employed to prepare it. There are numerous methods of preparing thin films of metal oxide and sulphide materials such as spray pyrolysis [*Jeyaprakash et al.,* 2010], atomic layer deposition [*Kim and Steven,* 2010], successive ionic layer adsorption and reaction [*Ghosh et al.,* 2008], and chemical bath deposition [*Nair and Nair*, 1991]. However, during the deposition process, many other related phases are likely to form: $SnS_2$. $Sn_2S_3$ and $Sn_3S_4$ [*Calixto-Rodriguez et al.,* 2009]. The chemical bath deposition method is an economic and efficient method for preparing thin films of SnS. This method

does not require vacuum conditions and hence is appropriate for basic research [*Ristov et al.,* 1989**]**. In this work, we have prepared thin films of SnS using this method and investigated the influence of concentration of TEA in the precursor solution and the annealing temperature towards the optical energy band gap measurement of the films on glass substrate. The structure of the film was studied by using X-ray diffraction technique. The optical absorption properties were determined by using a UV-Visible Spectrophotometer.

## 2. Experimental

Thin films of SnS were deposited using a chemical bath deposition at room temperature. The precursor solution was prepared by mixing equal volumes of 0.1M stannous chloride, ($SnCl_2 \cdot 2H_2O$) and 0.1M thioacetamide (TA), 15ml of Triethanolamine (TEA) and 8ml of ammonia (25% $NH_3$) and distilled water [*Pramanik et al.,* 1987] . All the chemicals used were of analytical grade. Ultrasonically cleaned glass substrates were vertically dipped into the as-prepared bath solution at room temperature (26$^o$C) for 22 hours. Then, the substrates were taken out, rinsed with distilled water and dried in air. The structural properties of the as-prepared films were studied using a Rigaku diffractometer with $CuK_\alpha$ radiation of wavelength, λ= 1.54056 Angstrom (Å). The optical transmittances (T %) of the deposited thin films were measured with an Ocean Optics USB 2000 Spectrophotometer, Singapore. This transmittance data was utilized to plot $(\alpha h\nu)^2$ versus hν and $(\alpha h\nu)^{1/2}$ versus hν and hence calculated the direct and indirect optical band gap ($E_g$) of SnS thin films [*Jeyaprakash et al.,* 2009].

## 3. Results and Discussions

The deposited thin films were uniform and dark brown in color. Figure 1 depicts the X-ray diffraction pattern of the as-prepared thin film. Three major peaks were observed at 2θ = 26.6116$^o$, 30.7920$^o$, and 44.0935$^o$ respectively. Table 1 shows the corresponding d-spacing values and (hkl) plane orientation with reference to JCPDS card no. 83-1758 [*Ghosh et al.,* 2008]. It shows that the peak at 2θ = 26.6116$^o$ corresponding to d = 3.3469Å of (021) orientation, 2θ = 30.7920$^o$ corresponding to d = 2.9014Å of (040) orientation, and 2θ = 44.0935$^o$ corresponding to d = 2.0521 Å of (200) orientation. The result confirms that the deposited material was SnS film of polycrystalline and orthorhombic in structure. The crystallite size (D) of the SnS film was calculated using Debye Scherrer's formula, $D = 0.9\lambda/\beta\cos\theta$ where λ is the wavelength of X-ray used and β is full width half maximum

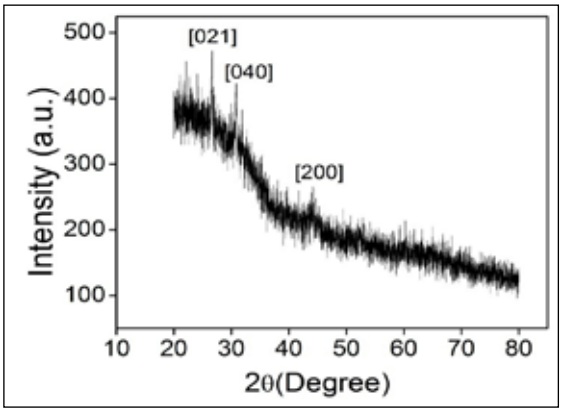


**Figure 1**. X-ray diffraction pattern of SnS film prepared at room temperature.

(FWHM) measured in radian and θ is the Bragg angle [*Guneria et al.,* 2010 ]. The average value of crystallite size of SnS film was found to be 320 Å.

Figure 2(a) shows the transmittance curves of SnS films prepared with different concentrations of TEA at room temperature captured in the wavelength range 400-1300 nm. The maximum transmittance of about 60% above the fundamental edges was observed with 6ml of TEA. As the concentration of TEA decreased the transmittance was found to be increasing for the studied range of samples, it may be due to presence of higher band gap phase in the film. To determine the energy gap values, we plotted the graphs of $(\alpha h\nu)^{2}$ versus hν and $(\alpha h\nu)^{1/2}$ versus hν which was shown in Figure 2b and Figure 2c respectively. The band energies were determined by extrapolating the straight line portion of the plots to intersect the hν axis [*Jeyaprakash et al.,* 2009]. The direct and indirect energy band gaps for samples prepared with 15ml of TEA and 8ml of $NH_3$ were found to be 1.76 eV and 0.89 eV respectively. Figure 2b showed the variation of direct band gap energy with TEA concentration. It was increased from 1.76eV to 2.11eV when we decreased the concentration of TEA from 15ml to 6ml. Following the same trend, Figure 2c showed that the indirect energy gap increased from 0.89 eV to 1.38eV for the same decrease of TEA concentration from 15ml to 6ml. Figure 2d shows the variation of $(\alpha h\nu)^2$ with photon energy hν and observed energy values when the sample prepared with 12ml of TEA was heated from room temperature to 400° C. The band gaps were found to be 1.79eV, 2.00eV, 2.30eV, and 3.32 eV at RT, 200°C, 300 °C, and 400 °C respectively. Annealing the film at high temperatures possibly changes their phases from SnS to binary sulfides: $SnS_2$ or $Sn_2S_3$, $Sn_3S_4$, and $SnO_2$ [*Guneria et al.,* 2010]. The inset shows the direct band gap of 3.32eV measured at 400°C. In the figures 2a through 2c the symbols: black filled squares, red filled circles, green filled up triangles, blue filled down triangles represent the SnS films prepared with 15 ml, 12ml, 10ml, and 6ml of TEA respectively. In figure 2d, the symbols: black filled squares, red filled circles, blue filled up triangles, dark cyan filled down triangles represent the SnS film prepared with 12ml of TEA but annealed at room temperature, 200°C, 300°C, and 400°C respectively.

## 4. Conclusions

Thin films of tin sulphide were deposited on glass substrate at room temperature using chemical bath deposition. The X-ray analysis confirmed that the deposited material was SnS with polycrystalline and orthorhombic structure.

**Table 1.** 2θ, observed and JCPDS d-spacing, (hkl) values, FWHM, and grain size of SnS film

| S. N. | 2θ ( Deg) | Observed d-spacing (Å) | JCPDS d-spacing (Å) | (hkl) | FWHM in degree | Grain Size D(Å) | JCPDS File No. |
|---|---|---|---|---|---|---|---|
| 1. | 26.6116 | 3.3469 | 3.3774 | (021) | 0.2574 | 317 | 83-1758 |
| 2. | 30.7920 | 2.9014 | 2.8707 | (040) | 0.1608 | 512 | |
| 3. | 44.0935 | 2.0521 | 2.0740 | (200) | 0.6494 | 132 | |

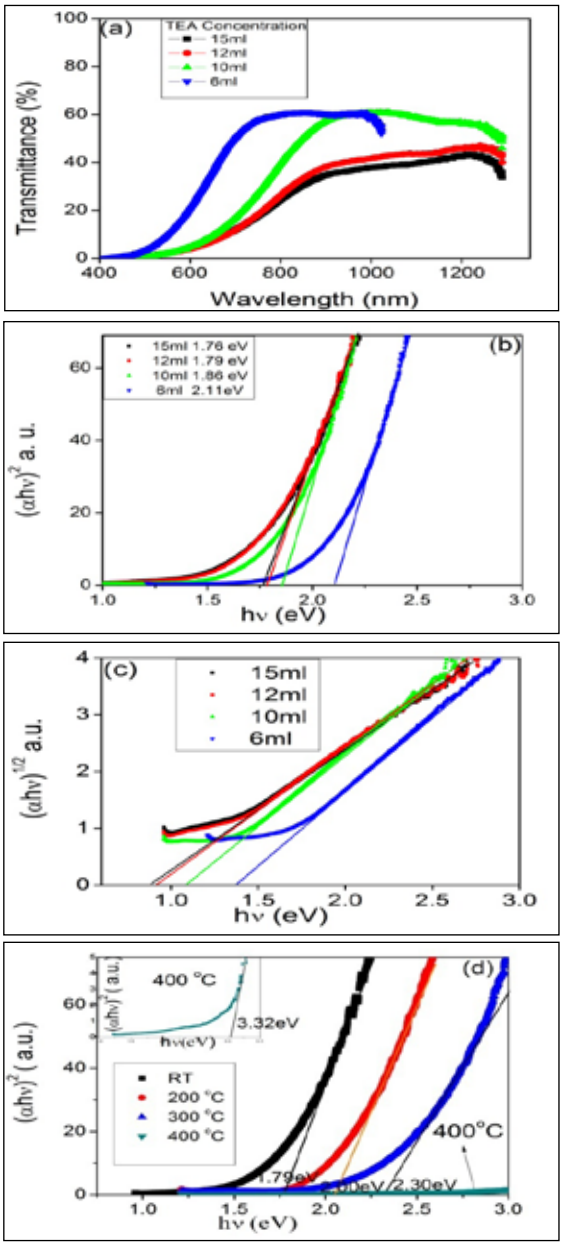


**Figure 2**. (a) Transmittance, T % versus wavelength (b) Plot of $(\alpha h\nu)^2$ versus hν (c) Plot of $(\alpha h\nu)^{1/2}$ versus hν for samples prepared with different concentration of TEA (d) variation of direct band gap with temperature for sample prepared with 12ml of TEA in the parent solution, inset to the figure shows plot for the sample annealed at 400°C.

The average crystallite size of SnS was found to be 320Å. The direct and indirect energy gap of as-prepared SnS film prepared with 15ml of TEA and 8ml of $NH_3$ at room temperature were found to be 1.76 eV and 0.89 eV respectively. The effect of TEA concentration on band gap measurement concluded that the direct and indirect band gap increased with the decrease in concentration of TEA. Annealing the sample showed that increase in direct band gap values from 1.79 eV to 3.32eV for the rise of temperature from room temperature to 400°C, which may be due to change of phase from a mixture of SnS-$SnS_2$ to SnS-$SnO_2$ [*Calixto-Rodriguez et al.*, 2009].

## Acknowledgment

Authors would like to thank Government of Nepal, Ministry of Science and Technology, Singh Durbar, Kathmandu, Nepal for providing financial support for this project. Editor N. P. Chapagain thanks referees for their help in evaluating this paper

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